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ELECTRONIC SUPPLEMETARY INFORMATION

Reversible transformation between Cu(I)-thiophenolate coordination polymers displaying luminescence and electrical properties

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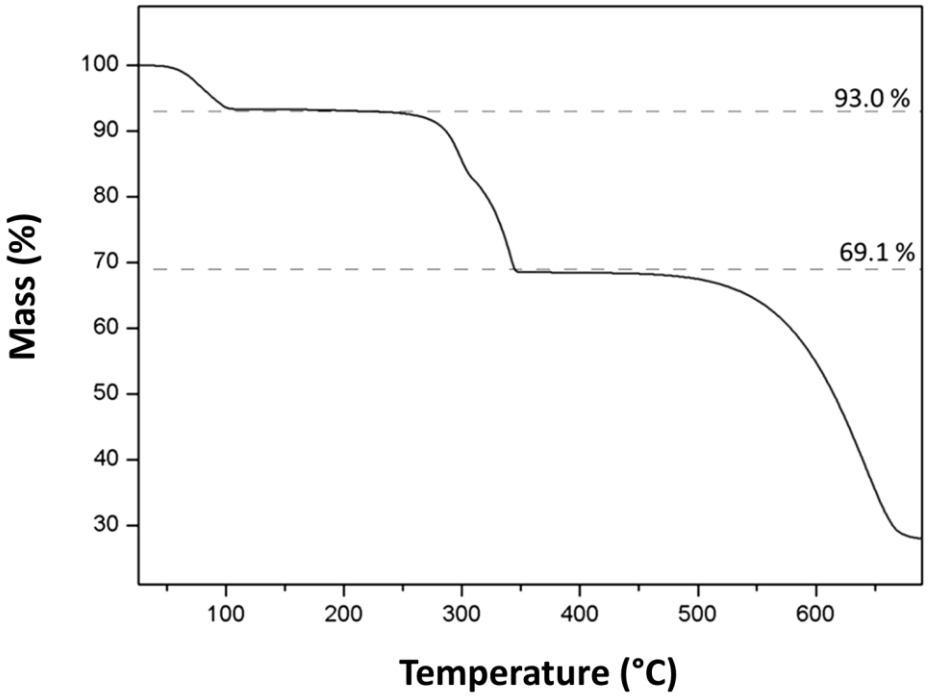

Fig. S1. TGA curve of **1** under N_2 atmosphere at a heating rate of 5 °C min^{-1}. The dashed lines indicate the expected weight changes for the proposed transformations.

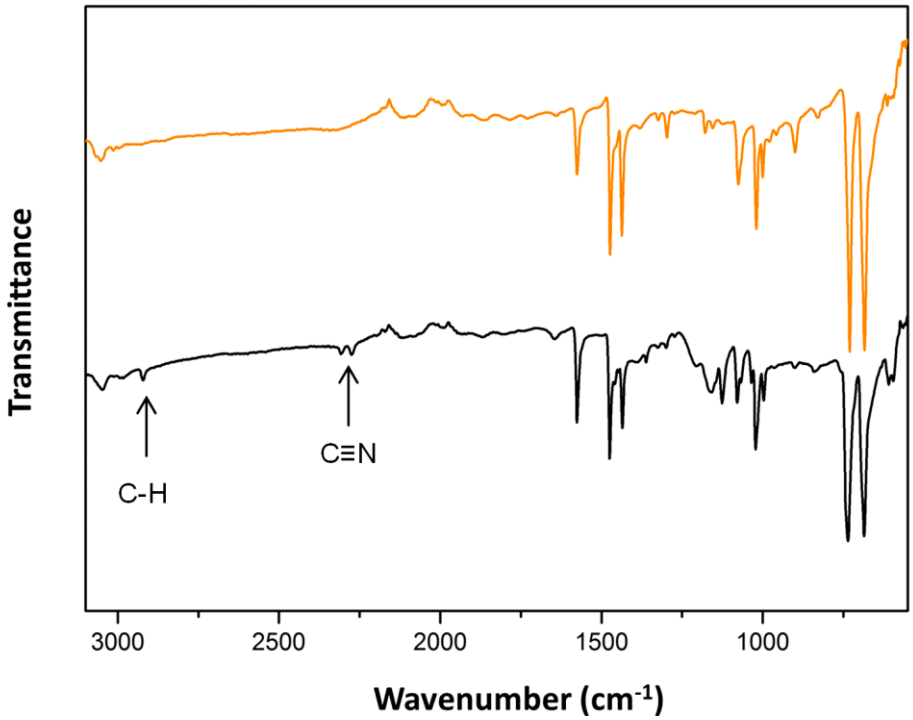

Fig. S2. FT-IR spectra of polycrystalline solid sample of **1** before heating (black) and after heating at 140 °C under argon atmosphere for 30 min (orange) in KBr pellets.

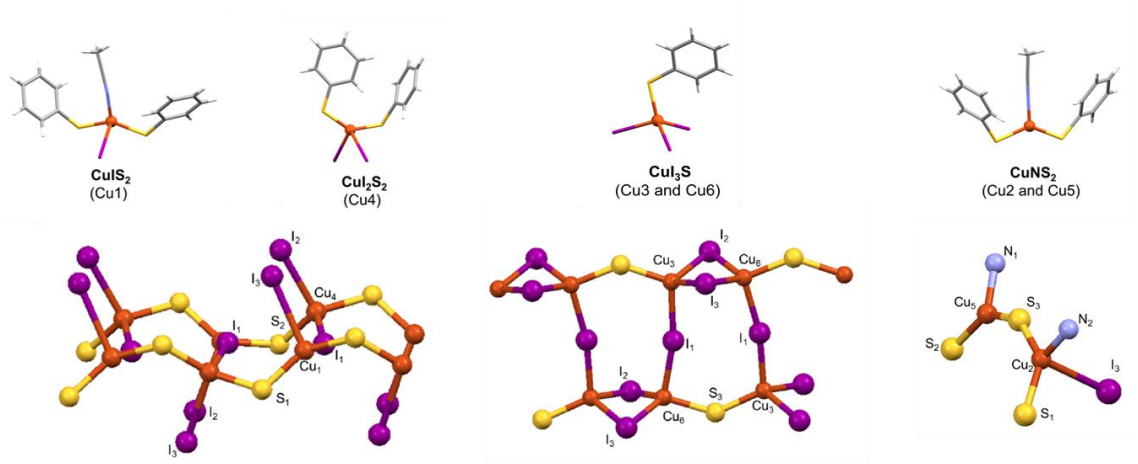

Fig. S3. Coordination environments around the different copper(I) atoms in **1**.

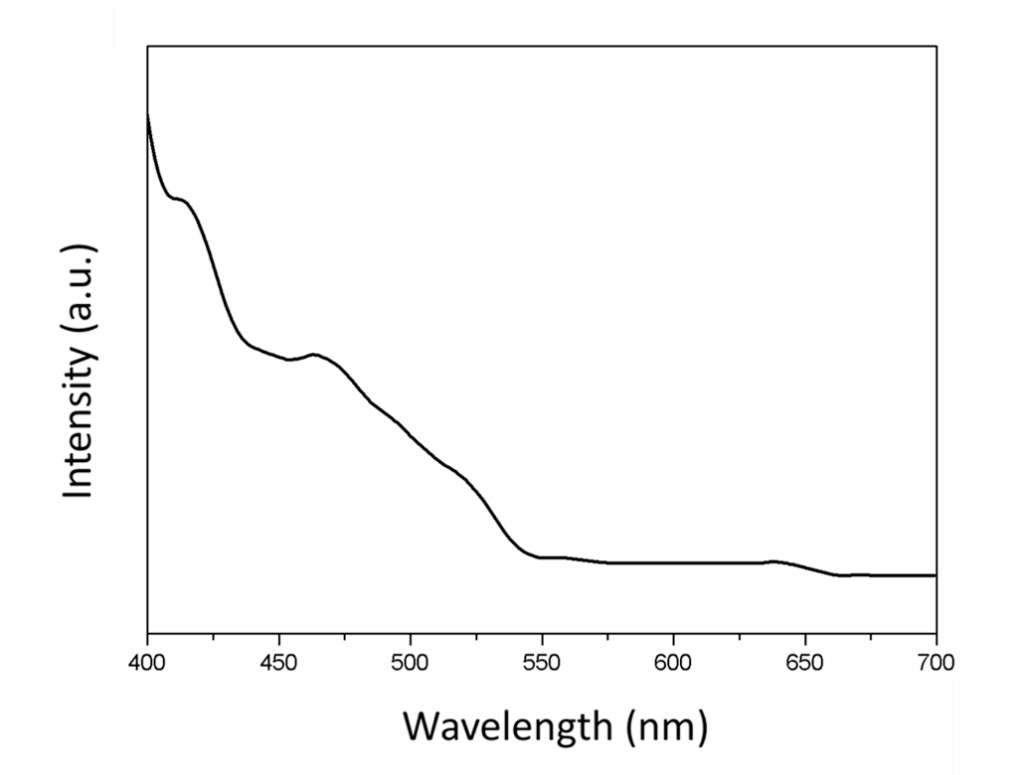

Fig. S4. Emission spectra of thiophenol (TP) upon excitation at 359 nm at room temperature.

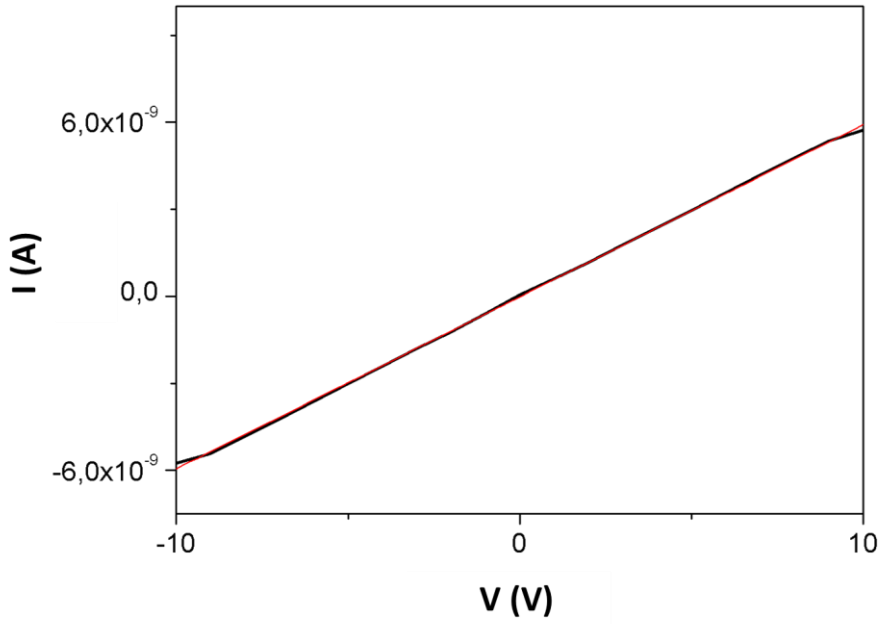

Fig. S5. Intensity (A) *versus* voltage (V) (black) and linear fit (red) corresponding to one pressed pellet of compound **1**, measured with the two-contact method, with graphite paint at 300 K.

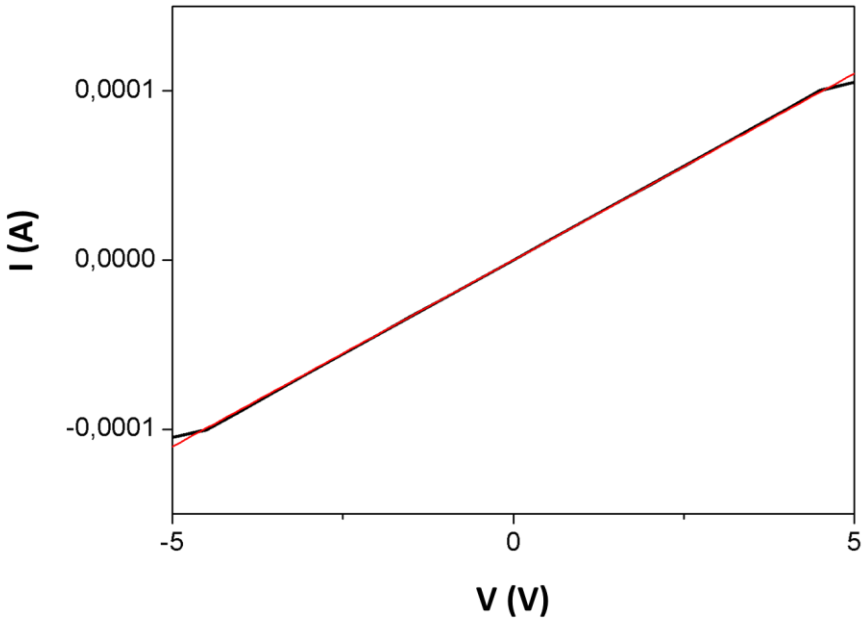

Fig. S6. Intensity (A) *versus* voltage (V) and linear fit (red) corresponding to one pressed pellet of compound **2**, measured with the two-contact method, with graphite paint at 300 K.

Table S1. Copper environment distances (Å) in **1**

Cu1—S1	2.258(2)
Cu1—S1^{i}	2.240(2)
Cu1—I1	2.6491(14)
Cu2—N2	1.977(9)
Cu2—S1	2.230(2)
Cu2—S3^{ii}	2.279(3)
Cu3—S3^{ii}	2.334(3)
Cu3—I1	2.6903(15)
Cu3—I2^{i}	2.7066(16)
Cu3—I3^{i}	2.7343(16)
Cu4—S2	2.262(3)
Cu4—S2^{ii}	2.282(2)
Cu4—I1	2.6869(14)
Cu4—I2^{i}	2.9062(16)
Cu5—N1	1.986(9)
Cu5—S2	2.223(3)
Cu5—S3	2.269(3)
Cu6—S3	2.354(3)
Cu6—I1	2.6494(14)
Cu6—I2	2.6729(16)
Cu6—I3	2.6635(16)
Cu2···Cu3	2.883(2)
Cu3···Cu5^{ii}	2.934(2)
Symmetry codes: (i) x, 3/2−y, −1/2+z; (ii) x, 3/2−y, 1/2+z.	

Table S2. Copper environment angles (°) in **1**

S1—Cu1—S1^{i}	139.46(12)
S1—Cu1—I1	99.45(7)
S1^{i}—Cu1—I1	108.48(8)
N2—Cu2—S1	118.1(3)
N2—Cu2—S3^{ii}	105.8(3)
S1—Cu2—S3^{ii}	132.79(10)
S3^{ii}—Cu3—I1	111.56(7)
S3^{ii}—Cu3—I2^{i}	120.20(8)
S3^{ii}—Cu3—I3^{i}	114.34(8)
I1—Cu3—I2^{i}	103.65(5)
I1—Cu3—I3^{i}	103.22(5)
I2^{i}—Cu3—I3^{i}	101.96(5)
S2—Cu4—S2^{ii}	133.30(11)
S2—Cu4—I1	106.20(8)
S2—Cu4—I2^{i}	109.25(8)
S2^{ii}—Cu4—I1	98.00(7)
S2^{ii}—Cu4—I2^{ii}	105.71(7)
I1—Cu4—I2^{ii}	98.60(5)
N1—Cu5—S2	116.8(3)
N1—Cu5—S3	106.9(3)
S2—Cu5—S3	136.31(10)
S3—Cu6—I1	97.82(7)
S3—Cu6—I2	117.17(8)
S3—Cu6—I3	119.88(8)
I1—Cu6—I2	106.39(5)
I1—Cu6—I3	109.82(5)
I2—Cu6—I3	104.77(5)
Symmetry codes: (i) x, 3/2−y, −1/2+z; (ii) x, 3/2−y, 1/2+z.	

Table S3. Copper environment distances (Å) in **2**

Cu1—S1	2.2982(19)
Cu1—S1^{i}	2.2697(16)
Cu1—S1^{ii}	2.3033(16)
Symmetry codes: (i) 1/2-y,x,-1/2-z; (ii) 1/2-y,x,1/2-z.	

Table S4. Copper environment angles (°) in **2**

S1—Cu1—S1^{i}	112.87(4)
S1—Cu1—S1^{ii}	133.47(5)
S1^{i}**—Cu1—S1**^{ii}	113.61(7)
Cu1—S1—Cu1^{iii}	97.61(9)
Cu1—S1—Cu1^{iv}	79.95(8)
Cu1^{iii}**—S1—Cu1**^{iv}	113.61(6)
Symmetry codes: (i) 1/2-y,x,-1/2-z; (ii) 1/2-y,x,1/2-z; (iii) y,1/2-x,-1/2-z; (iv) y,1/2-x,1/2-z.	

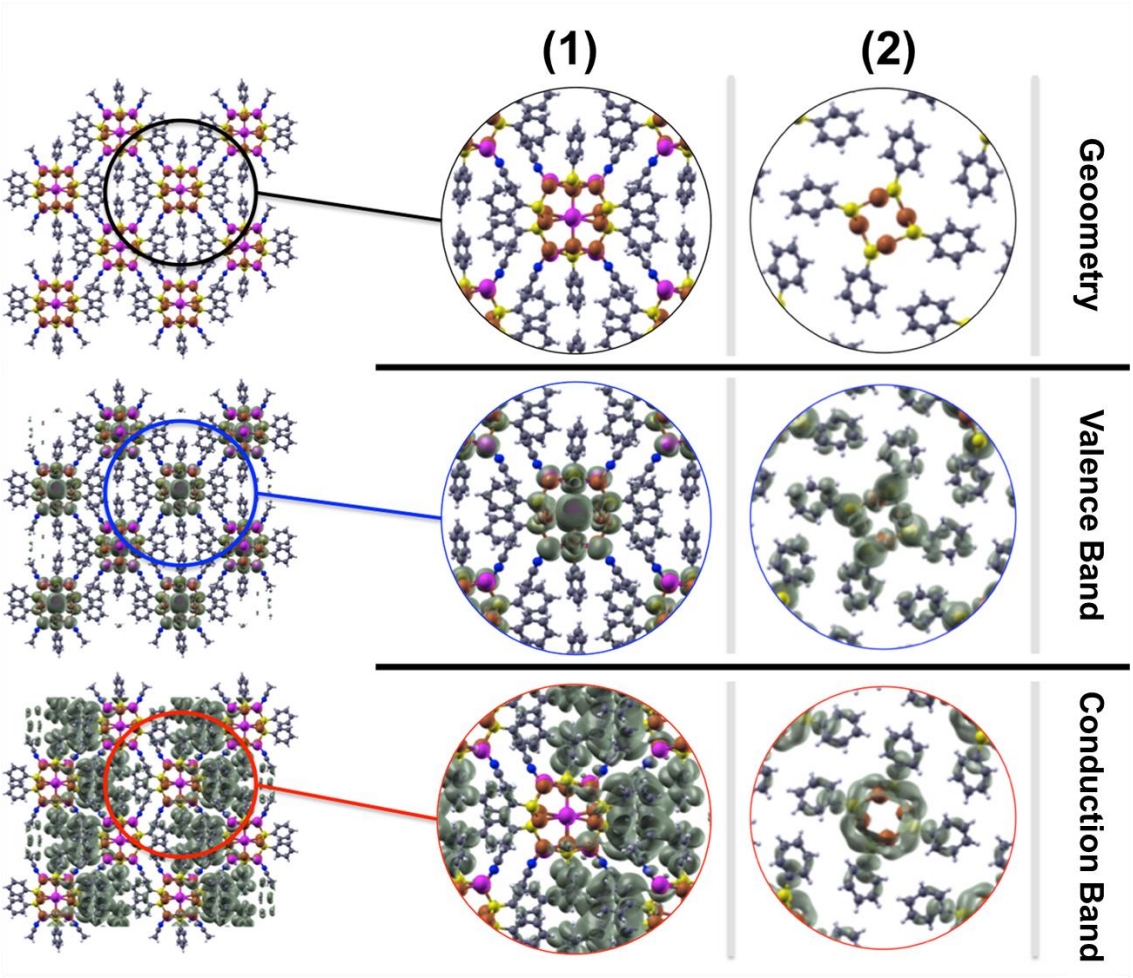

Fig. S7. Computed valence (middle panels) and conduction (bottom panels) band orbital electron isodensities (10^{-4} e^{-} $Å^{-3}$) for the compounds **1** and **2**. Clean geometries are also shown for a better visualization (top panels).

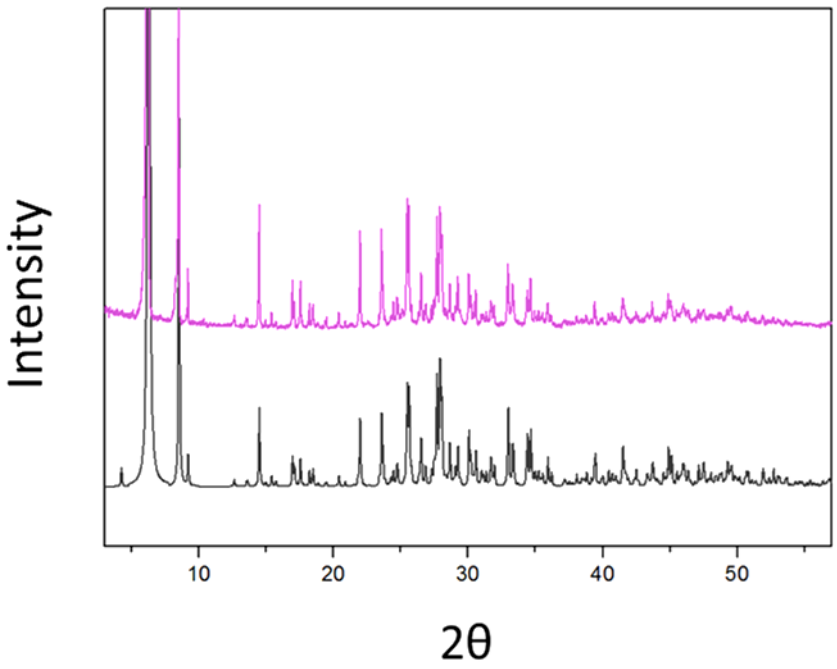

Fig. S8. Experimental (purple) and simulated (black) XRPD patterns of $[Cu_6I_3(TP)_3(MeCN)_2]_n$ (**1**).

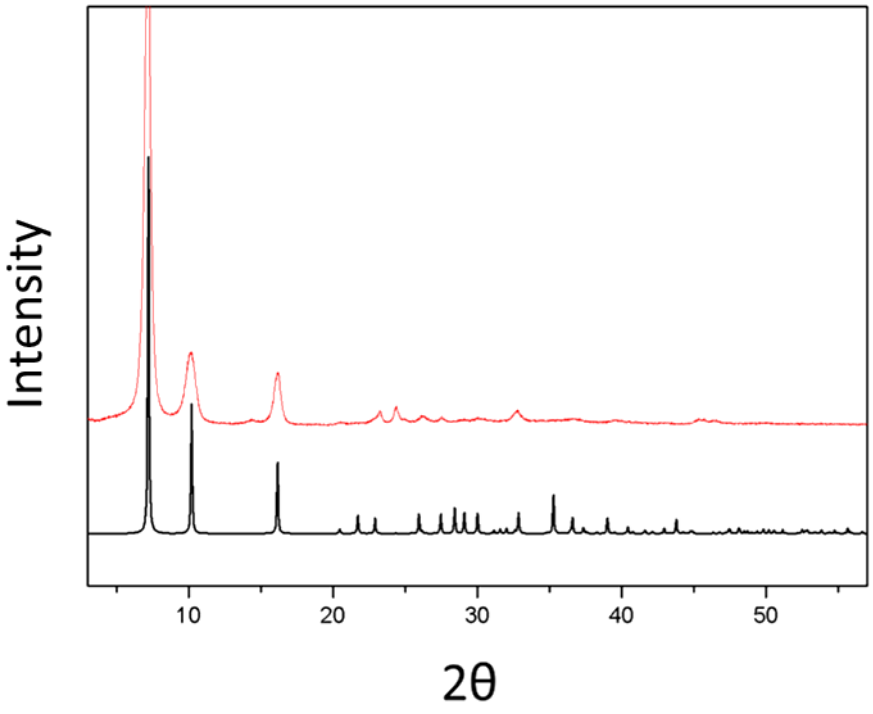

Fig. S9. Experimental (red) and simulated (black) XRPD patterns of $[Cu(TP)]_n$ (**2**).

File in CIF format for compounds 1 and 2 [CCDC 1504677–1504680 and 1566448].
For crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ce00313d